



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) EP 1 006 570 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
07.06.2000 Bulletin 2000/23

(51) Int. Cl.⁷: H01L 21/3205, H01L 21/311,
H01L 21/3213

(21) Application number: 99309263.4

(22) Date of filing: 22.11.1999

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 03.12.1998 US 204706

(71) Applicants:
• SIEMENS AKTIENGESELLSCHAFT
80333 München (DE)
• International Business Machines Corporation
Armonk, NY 10504 (US)

(72) Inventors:
• Ramachandran, Ravikumar
Beacon, NY 12508 (US)

• Gutsche, Martin
Poughkeepsie, NY 12603 (US)
• Natzie, Wesley
New Paltz, NY 12561 (US)
• Akatsu, Hiroyuki
Yorktown Heights, NY 10598 (US)
• Yu, Chien
Highland Mills, NY 10930 (US)

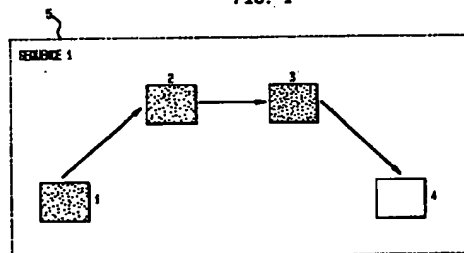
(74) Representative:
Vigars, Christopher Ian et al
Haseltine Lake & Co.,
Imperial House,
15-19 Kingsway
London WC2B 6UD (GB)

(54) Removal of post-rie polymer on Al/Cu metal line

(57) A method for removal of post reactive ion etch sidewall polymer rails on a Al/Cu metal line of a semiconductor or microelectronic composite structure comprising:

- 1) supplying a mixture of an etching gas and an acid neutralizing gas into a vacuum chamber in which said composite structure is supported to form a water soluble material of sidewall polymer rails left behind on the Al/Cu metal line from the RIE process; removing the water soluble material with deionized water; and removing photo-resist from said composite structure by either a water-only plasma process or a chemical down stream etching method; or
- 2) forming a water-only plasma process to strip the photo-resist layer of a semiconductor or microelectronic composite structure previously subjected to a RIE process;
- 3) supplying a mixture of an etching gas and an acid neutralizing gas into a vacuum chamber on which said structure is supported to form a water soluble material of saidwall polymer rails left behind on the Al/Cu metal line from the RIE process; and
- 4) removing the water soluble material with deionized water.

FIG. 1



EP 1 006 570 A1

Description

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

[0001] The invention relates to a improved process for removing post-RIE polymer rails formed on a Al/Cu metal line of semiconductor structures or microelectronic devices using a chemical mixture that contains an etching gas and an acid neutralizing gas. More specifically, the improvement process comprises removing the sidewall polymers left behind after the metal (Al/Cu) RIE process, using a mixture of an etching agent and an acid neutralizing reactant introduced either in a gaseous or plasma form, wherein the etching agent is a fluorine based species such as HF, and the acid neutralizing reactant is a chemical such as NH_3 .

2. DESCRIPTION OF THE PRIOR ART

[0002] In ULSI (ultra large scale integration) devices, the electrical connection between metal layers is achieved by sub micron via holes. These via holes are formed by cutting through interlayer dielectric (ILD) using anisotropic reactive ion etching (RIE) processes, usually with CF_4 or CHF_3 and with inert gas mixtures. The etch residue is non-corrosive and is easily removed.

[0003] During the RIE process of a composite structure having silicon oxide as the interlayer dielectric, a barrier layer, a metal stack layer, and a photo-resist, after exposure and development of the photo-resist, insoluble polymers that are mostly inorganic in nature form as sidewalls and some of the chemical constituents are Al, Si, Ti, O, C and Cl. This residue is relatively corrosive and difficult to remove.

[0004] Currently, post metal RIE cleaning is done using a chromic-phosphoric acid tank bath or by other solvent based chemistry. Further, there is a certain time window of approximately 4 hours between completion of the RIE process and the wet cleaning step to avoid corrosion.

[0005] Some drawbacks of the currently existing wet chemical cleaning methods are as follows:

- 1) An acid based chemistry (without any HF in it) is not efficient in removing polymer rails that have high silicon content in them (as found in metal pads located in the support region); and
- 2) A solvent based chemistry generally takes a longer process time (approximately 10 minutes as compared to 2 to 4 minutes for a typical acid based clean) and typically is encumbered as a result of costs and environmental disposal requirements.

[0006] An apparatus for and method of accurately using a gaseous mixture of HF and NH_3 to etch precise

amounts of silicon dioxide is disclosed in U.S. Patent 5,282,925. This method comprises: admitting a reactant containing gas into a vacuum chamber onto a substrate having a material to be etched to form a film of the reactant on the surface of substrate material; controlling the composition and residence time of the film on the surface of the material to be etched in an amount accurate of material on the substrate; and removing any unwanted reactant and reaction product from the chamber or surface of the substrate. The patent does not teach reaction with a complex mixture of silicon dioxide, aluminum dioxide, and carbon, or successful diffusion of ammonia and HF through the reaction products of the complex mixture.

[0007] U.S. Patent 5,129,958 discloses a method for cleaning a CVD deposition chamber in a semiconductor wafer processing apparatus comprising, contacting fluorine residues remaining therein from a plasma fluorine cleaning step with one or more reducing gases.

[0008] Pages 235-242 of the Electrochemical Society Proceedings Volume 95-20 by Tong et al., discloses removal of polymeric/silicate residues and reduction of contact resistance for inter-metal via holes by vapor phase HF cleaning. The vapor HF treatment reduces the metal-to-via contact resistance, due to the presence of AlF_3 , formed by the reaction between the vapor HF and the $\text{Al}/\text{Al}_2\text{O}_3$ at the via base. CF_4 or CHF_3 based RIE chemistry on an oxide field produces a polymer of low aluminum content without chlorides. Such a polymer is easily removed and is less corrosive than the one formed after aluminum RIE.

[0009] A process for removal of residues remaining after etching a polysilicon layer in formation of an integrated circuit structure is disclosed in U.S. Patent 5,296,093, wherein, in lieu of removing polymerized silicon/oxide-containing residues by dipping previously RIE etched structure into a HF bath, the RIE etched structure is treated with an aqueous ammonium-containing base/peroxide solution after completion of the RIE etch to remove such residues.

[0010] There is a need in the art of cleaning RIE etched materials to lessen the time window of about 4 hours between the completion of the RIE process and the wet clean step.

[0011] Putting it another way, there is a need to avoid the time coupling between RIE and wet clean and to avoid the use of a wet chemical clean in the art of reactive ion etching (RIE) processes which form metal lines by cutting through metal stack by virtue of anisotropic reactive ion etching (RIE) processes.

SUMMARY OF THE INVENTION

[0012] It is therefore desirable to remove post-RIE polymer rails formed on a Al/Cu metal line by employing a mixture of etching gas and an acid neutralizing gas as a gas clean.

[0013] One embodiment of the present invention

can provide a metal etched post clean process that does not involve the use of wet chemicals.

[0014] Another embodiment of the present invention can provide a post metal etch process by using a gas phase chemistry that eliminates both the use of wet chemicals by using only deionized water (DIW) and the time window or span that currently exists between a metal etch and clean.

[0015] Another embodiment of the present invention can provide removal of post-RIE polymer rails formed on a Al/Cu metal line by using gas phase chemistry that uses a fluorine based etching agent such as HF and an acid neutralizing chemical such as NH_3 .

[0016] Another embodiment of the present invention can provide a process for removal of post-RIE polymer rails on the metal line of Al/Cu by chemically modifying the polymer rails into a water-soluble form by a gas mixture of HF and NH_3 and then remove the water soluble form of the polymer rails using a deionized water rinse.

[0017] Another embodiment of the present invention can suppress the corrosion of the metal Al/Cu line by removing the post-RIE polymer rails by neutralizing the active chloride component in the rails that causes corrosion by either neutralizing the chloride component with NH_3 or exchanging the chloride component with fluoride.

[0018] Another embodiment of the present invention can effect removal of the post-RIE polymer rails formed on a Al/Cu metal line by using integrated process that eliminates both the use of post wet chemical and the time delay involved between the RIE and the wet clean step, and thereby streamline the production process at the metal etch level.

[0019] In general, embodiments of the invention can be accomplished by avoiding the time coupling between RIE and wet clean and the use of a wet chemical clean, by introducing a mixture of an etching agent and an acid neutralizing reactant, either in a gaseous or a plasma form, after the metal etch process, to chemically modify into a water soluble form, the post-RIE polymer rails and thereby suppressing the corrosion of the metal line, eliminating the time coupling between RIE and wet clean, and also eliminating the use of the wet chemical clean as well.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020]

Figure 1 is a block diagram of an embodiment of the present invention;

Figure 2 is a block diagram of an alternative embodiment of the present invention;

Figures 3 and 4 are microphotographs showing results from the embodiments of Figures 1 and 2 respectively.

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

[0021] FIG. 1 is a block diagram showing sequence 1 of the present invention, wherein, from sequence 1, the RIE polymers are first converted into a water soluble chemical form in step 2, and during step 3, the RIE polymers in water soluble chemical form are removed. At step 4, the remaining photo-resist is removed by either a plasma process or a chemical down stream etching method. Since this step usually takes place at temperatures greater than 200°C , a passivation layer forms on the Al metal line surface. As shown in Figure 1, the sequence of steps illustrated can take place within integrated metal etch tool 5 which provides RIE of metal lines, removal of photoresist, removal of sidewall residues and associated processing.

[0022] FIG. 2 is a block diagram which can take place within tool 5, depicting an alternative embodiment of the invention, wherein, step 2 is used to remove the photo-resist in the strip chamber. This process is done with a water-only plasma at a low temperature of about $175\text{--}200^\circ\text{C}$ thereby limiting the thickness of the sidewall polymer. The polymer rails are chemically modified in step 3 and rinsed off with DIW in step 4.

[0023] FIG. 3 are microphotographs showing the array and support region photos resulting from the process of sequence 1, where a mixture of $\text{HF}+\text{NH}_3$ is used to remove polymer rails of BCl_3 RIE etching of an Al/Cu metal line, followed by rinsing and plasma stripping of polymer.

[0024] FIG. 4 is a microphotograph of an alternative embodiment or sequence 2 of the invention wherein, photos of the array and support region are shown as a result of removing polymer rails of BCl_3 RIE etching of an Al/Cu metal line followed by a water based downstream plasma and, after subjecting said rails to a mixture of $\text{HF}+\text{NH}_3$ and rinsing.

[0025] The foregoing and other objects and advantages of the invention will be better understood by resort to the following detailed description of the preferred embodiments of the invention.

[0026] After the metal etch process, a gas phase chemistry is utilized to eliminate both the use of wet chemicals by using only deionize water (DIW) and the time window that exists between the metal etch and clean.

[0027] Further, an embodiment can provide a method for integrating the use of the gas phase chemistry with the metal etch tool is provided, wherein the gas phase chemistry uses a fluorine based etching agent such as HF and an acid neutralizing chemical, such as NH_3 .

[0028] Through experimentation, it was discovered that the Al, Ti, and C in the complex sidewall mixture following metal RIE do not inhibit the reaction of ammonia and HF with silicon dioxide nor do they inhibit diffusion of ammonia and HF through the solid reaction product

which is formed. The post-RIE polymer rails on the Al/Cu metal line are first chemically modified into a water soluble and less corrosive form by the gas mixture, which is then removed using a deionized water rinse.

[0029] While not desirous of being bound by any theory as to how the invention is accomplished, it is nevertheless believed that the chlorine component in the polymer rails is the active species that enhances corrosion, and that the chloride part of the polymer rails (either as free Cl⁻ or HCl) is either neutralized with NH₃ or exchanged with fluoride, and that this chemical interaction is responsible for suppressing the corrosion of the Al/Cu metal line.

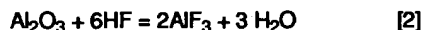
[0030] By use of a method embodying the present invention, the polymer rails are removed in an integrated process wherein, the metal etch-gas chemistry-DIW based clean, eliminates both the use of a post wet chemical and the time delay involved between the RIE and the wet clean step. Accordingly, this integrated invention process streamlines the production process of microelectronic devices at the metal etch level.

EXAMPLE 1

[0031] After the metal (Al/Cu) RIE process on a composite structure comprising a silicon oxide inter-layer dielectric, a barrier layer, a metal stack layer, and a photoresist layer, dry wall polymers rails remain that are mostly inorganic in nature, and some of the chemical constituents of the rails are Al, Si, Ti, O, C, and Cl.

[0032] Both the time coupling between RIE and wet clean and the use of a wet chemical clean is avoided by introducing into the reaction chamber, a mixture of an etching agent and an acid neutralizing reactant, either in a gaseous or in a direct or remote plasma form. The etching agent containing the fluoride based species is hydrofluoric acid and the acid neutralizing chemical is ammonia gas.

[0033] The etching agent reacts with the sidewall polymer rails and converts them into another chemical form that is easily removed, and the chemical reaction for this segment of the process is as follows:



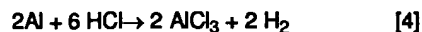
[0034] The acid neutralizing chemical effectively takes care of any acid species that may be present, such as HCl, which is the etchant gas used during the metal RIE process or that may form due to the reaction of free chlorides with water.

[0035] The neutralization reaction is as follows:



[0036] The products from both the etching and neu-

tralization reaction are soluble in deionized water. If the above reactions do not occur, then the sidewall can trap chlorine and water species. This could result in a corrosion cycle where the chlorine acts as a catalyst.



followed by a hydrolysis reaction,



with the HCl being cycled back to reaction [4].

[0037] These kinds of reactions give rise to the small time window between metal RIE and the sidewall removal which is needed for corrosion.

[0038] Reactions [1]-[3] are especially advantageous to prevent reactions [4]-[5], because gaseous H₂O is not required to induce the HF reaction with the oxides and because the low reaction pressure (under 10 mTorr) enables the H₂O reaction product to escape. The low reaction pressure also enable easy integration of a chamber designed to carry out reactions [1]-[3], with the metal RIE process tool. The vacuum chamber may be interfaced with the metal etch tool or could be left as a stand-alone chamber for introducing the reaction mixture.

[0039] Reference is now made to FIG 1, where step 1 of one embodiment of the invention involves the use of metal etch chemistry in which there is no change from existing methods (reactive ion etching [RIE]).

[0040] Accordingly, sequence 1 of the first embodiment of the invention involves the use of a metal etch well known in the prior art; however, step 2 of sequence 1 of the first embodiment as shown in FIG. 1, requires the gas phase chemistry in order to obtain the two sequences and the process integration wherein, after the RIE polymers are converted into a water-soluble chemical form by a mixture of HF and NH₃ to obtain a water soluble chemical. The water soluble chemical is rinsed in deionized water, whereupon the soluble chemical materials are removed. At step 4, the remaining photo-resist is removed by either a plasma process or a chemical down stream etching method. This step takes place at temperatures greater than about 200°C and a passivation layer forms on the aluminum metal line surface.

EXAMPLE 2

[0041] In this embodiment of the invention or sequence 2, step 1 involves the use of a metal etch chemistry such as that described in Example 1 on a composite structure comprising a silicon oxide inter-layer dielectric, a barrier layer, a metal stack layer, and a photoresist layer. At step 2 for sequence 2, a water-only plasma process is employed in the reaction chamber to strip the photo-resist; whereupon the formed polymer rails are chemically modified in step 3 by treatment with

a mixture of the hydrogen fluoride etching gas and the acid neutralizing gas, ammonia. Thereafter, deionized water is used to rinse off the water soluble chemical materials formed from the sidewall polymers in step 4.

[0042] It should be understood that, for the embodiments in both sequences 1 and 2 as shown in FIGS. 1 and 2, if necessary, an acid based clean may be used partly in the water rinse station to remove the residuals from the metal lines, and said acid based clean may be composed of a diluted sulfuric acid with hydrogen peroxide mixture. (Delehanty et al., Patent No. 5,780,363)

[0043] In the context of the invention, with the current trend towards the use of dielectric hard mask (silicon dioxide and silicon nitride layers), the integrated gas phase chemistry with the RIE process will be able to remove the polymer rails from the Al/Cu metal lines efficiently.

[0044] As can be seen from FIG. 3, microphotographs of X100K depict the array and support region of a DRAM chip obtained using a BCl_3 RIE etch that has been subjected to a mixture of $\text{HF} + \text{NH}_3$ and rinsed, followed by an oxidizing downstream plasma.

[0045] Similarly, in FIG. 4, the method of sequence 2 of the present invention depicts the array and support in which, after a BCl_3 RIE etch, the wafer is subjected to water downstream plasma followed by treatment with the gas phase chemistry combination of $\text{HF} + \text{NH}_3$, and thereafter rinsed to obtain the support. In FIG. 4, which shows the results of utilizing sequence 2 of the invention, the microphotographs are shown at X100K.

[0046] It is important to note that, the gaseous mixture of HF and NH_3 cannot be used to define the metal lines of Al/Cu. In order to form the Al/Cu metal lines, a chlorine based plasma chemistry is used. Typical sources of the chlorine based plasma are HCl/BCl_3 with Cl_2 gas.

[0047] The composite structure of the material giving rise to the metal lines of Al/Cu are as follows:

[0048] Silicon oxide as the interlayer dielectric, a barrier layer, a metal stack layer, and a photo-resist. After the exposure and development of the photo-resist, RIE is done to define the Al/Cu metal line. This leaves behind sidewall polymeric residues that have Al, Si, Ti, O, C and Cl, along with some amounts of the barrier layer elements as well.

[0049] In the present invention, the reason for using the particular gas or plasma mixture of HF and NH_3 is that is important to have a good process as a post-clean. In order to have a good process as a post-clean, it is necessary to remove the sidewall polymer which has chlorine in it to prevent enhancement of corrosion of the metal lines, and to etch/chemically modify the residue to be water soluble while simultaneously not etching the metal line itself.

[0050] Further, in the present invention, the NH_3 neutralizes most of the free chloride thereby preventing corrosion of the metal lines.

[0051] Once the chloride has been neutralized, the

HF/NH_3 then etches/chemically modifies and neutralizes the residue into a water soluble form.

[0052] The most significant advantage of the invention process is that it can be interfaced directly with the metal etched tool, where there is a separate chamber that performs this chemistry (either post resist strip or prior to resist strip), thereby allowing a final step of using only deionized water as a rinse.

[0053] Accordingly, subjecting the composite structure of silicon oxide as the inter layer dielectric, barrier layer, metal stack layer, and photo-resist layer to the etching/neutralizing gaseous or plasma mixture is a significant advance in the art of preparing microelectronic devices.

[0054] While it is to be noted that the preferred embodiments of the invention utilize a Al/Cu metal line in which post-RIE polymer rails formed are removed, it is to be understood that those skilled in the art may effect modifications, inclusive of practicing the invention for metal lines other than Al/Cu without departing from the spirit and scope of the invention.

Claims

1. A method for removal of post reactive ion etch sidewall polymer rails on a Al/Cu metal line of a semiconductor or microelectronic composite structure comprising:

supplying a mixture of an etching gas and an acid neutralizing gas into a vacuum chamber in which said composite structure is supported to form a water soluble material of sidewall polymer rails left behind on the Al/Cu metal line from the RIE process; removing the water soluble material with deionized water; and removing photo-resist from said composite structure by either a water-only plasma process or a chemical down stream etching method.

2. The method of claim 1 wherein said composite structure comprises a silicon oxide interlayer dielectric, a barrier layer, a metal stack layer, and a photoresist layer.
3. The method of claim 2 wherein said etching gas is HF and said acid neutralizing gas is NH_3 .
4. The method of claim 3 wherein removing said photo-resist accomplished at temperatures greater than 200°C .
5. The method of claim 1 wherein said mixture of said etching gas and said acid neutralizing gas is in the form of a plasma.
6. A method for removal of post ion etch sidewall polymer rails on a Al/Cu metal line of a semiconductor

or microelectronic composite structure comprising:

forming a water-only plasma process to strip
the photo-resist layer of a semiconductor or
microelectronic composite structure previously
subjected to a RIE process;
supplying a mixture of an etching gas and an
acid neutralizing gas into a vacuum chamber
on which said structure is supported to form a
water soluble material of sidewall polymer rails
left behind on the Al/Cu metal line from the RIE
process; and
removing the water soluble material with deion-
ized

15

water.

7. The method of claim 6, wherein the water-only
plasma process is conducted at temperatures
between about 175-275°C to limit the thickness of
the sidewall polymer. 20
8. The method of claim 7 wherein said composite
structure comprises a silicon oxide interlayer die-
lectric, a barrier layer, a metal stack layer, and a
photo-resist layer. 25
9. The method of claim 8 wherein said etching gas is
HF and said acid neutralizing gas is NH_3 . 30
10. The method of claim 6 wherein said mixture of said
etching gas and said acid neutralizing gas is in the
form of a plasma.
11. An integrated metal etch tool operable to perform 35
the method as recited in claim 6.
12. An integrated metal etch tool operable to perform
the method as recited in claim 7.

40

45

50

55

FIG. 1

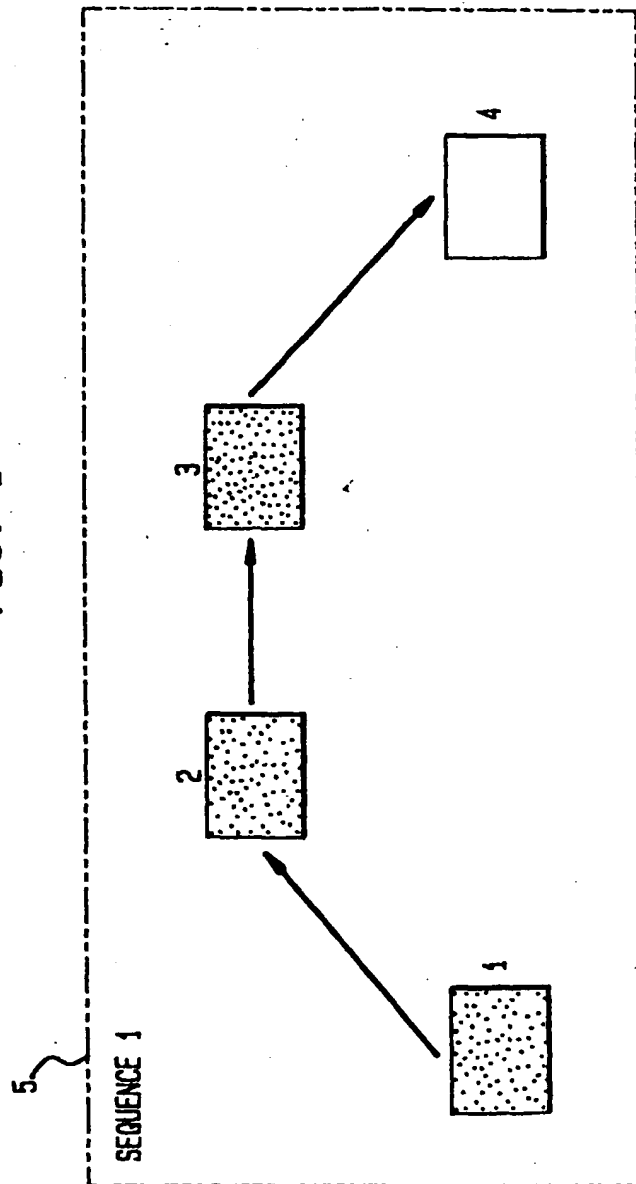


FIG. 2

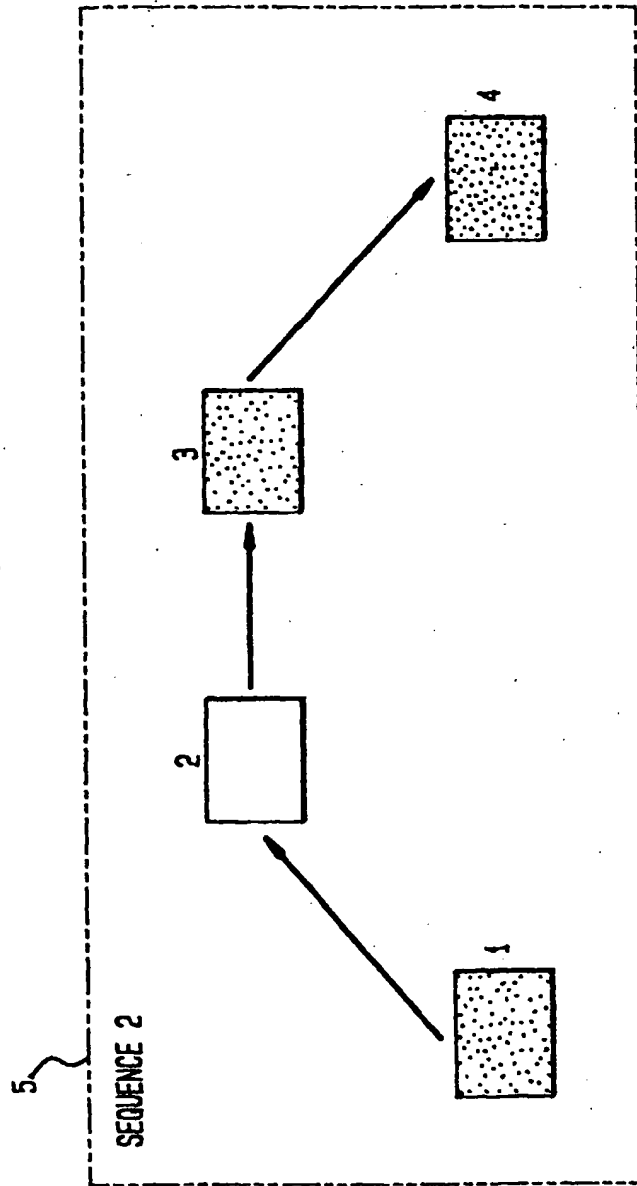


FIG. 3

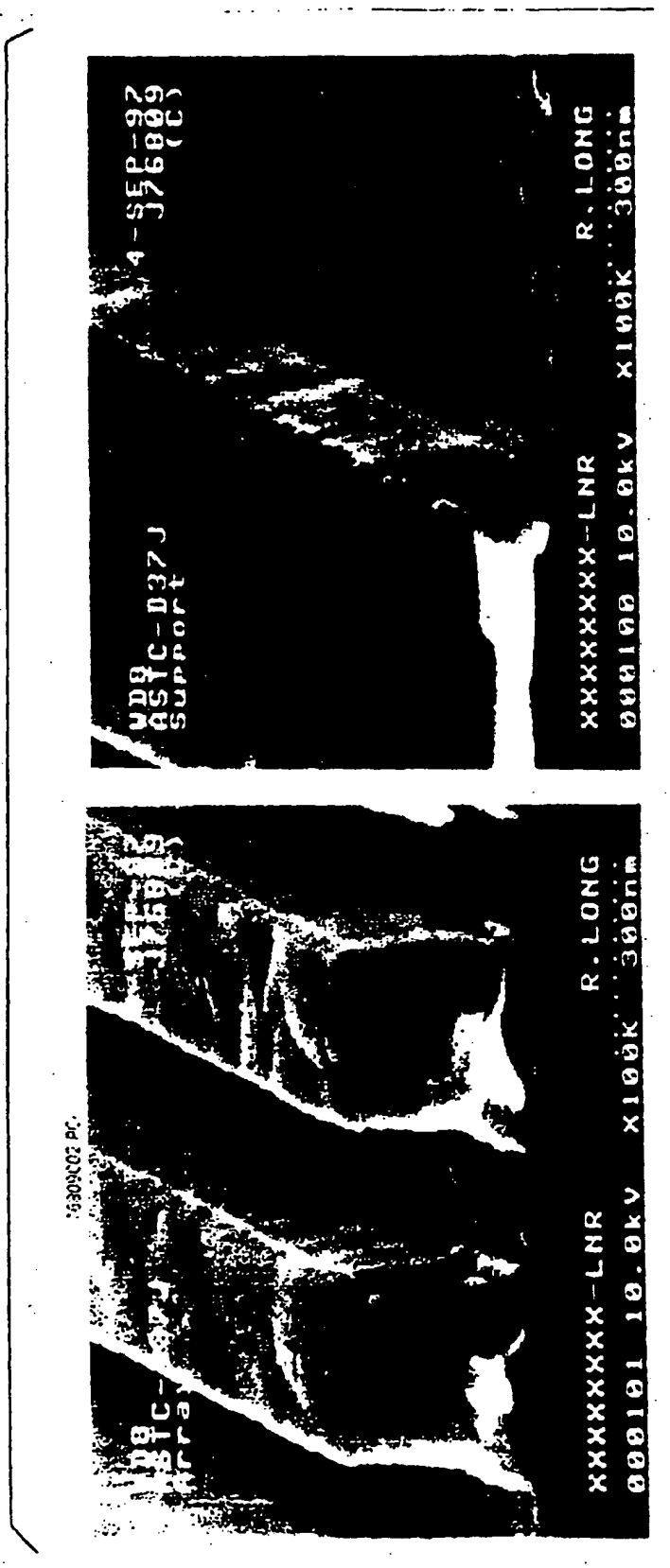
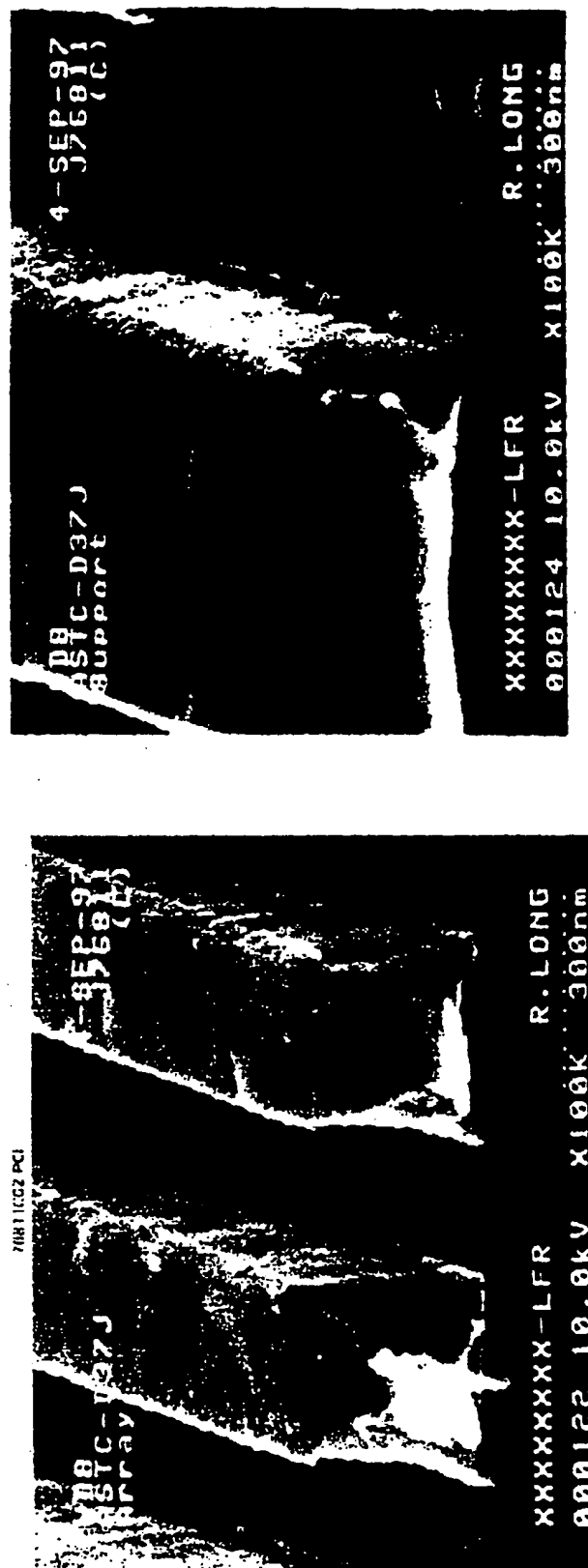


FIG. 4





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 30 9263

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
P,L, X	EP 0 957 512 A (SIEMENS AG ; IBM (US)) 17 November 1999 (1999-11-17) Priority * the whole document *	1-12	H01L21/3205 H01L21/311 H01L21/3213
X	EP 0 585 936 A (TEXAS INSTRUMENTS INC ; FSI INT INC (US)) 9 March 1994 (1994-03-09) * abstract; claim 1 *	1,2,6, 11,12	
A	---	8-10	
X	WO 96 36069 A (TEGAL CORP) 14 November 1996 (1996-11-14) * page 1, line 1 - page 3, line 18 *	11,12	
A	---		
A	EP 0 681 317 A (TEXAS INSTRUMENTS INC) 8 November 1995 (1995-11-08) * column 6, line 52 - column 7, line 15 *	3,9	
A	---		
A	US 5 685 951 A (TOREK KEVIN JAMES ET AL) 11 November 1997 (1997-11-11) * column 2, line 37 - line 43 *	3,9	

			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			H01L
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 28 March 2000	Examiner Le Meur, M-A
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 30 9263

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

28-03-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0957512 A	17-11-1999	US 5980770 A	09-11-1999
		CN 1238554 A	15-12-1999
		JP 11345805 A	14-12-1999
EP 0585936 A	09-03-1994	US 5348619 A	20-09-1994
		JP 7007002 A	10-01-1995
		US RE36006 E	22-12-1998
WO 9636069 A	14-11-1996	US 5672239 A	30-09-1997
		CA 2220046 A	14-11-1996
		CN 1184556 A	10-06-1998
		EP 0826231 A	04-03-1998
		JP 11505669 T	21-05-1999
EP 0681317 A	08-11-1995	JP 7302776 A	14-11-1995
		US 5494526 A	27-02-1996
US 5685951 A	11-11-1997	US 5990019 A	23-11-1999